ORO-5205-3

FOSSIL ENERGY

CHARACTERIZATION AND ANALYSIS OF DEVONIAN SHALES AS RELATED TO RELEASE OF GASEOUS HYDROCARBONS

Quarterly Technical Progress Report, March 1977—May 1977

M. Jack Snyder
J. R. Schorr

Date Published—May 31, 1977

Work Performed Under Contract No. EY-76-C-05-5205

Battelle
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161

Price: Paper Copy $4.00 (domestic)
$6.50 (foreign)
Microfiche $3.00 (domestic)
$4.50 (foreign)

Printed in the United States of America
USERDA Technical Information Center, Oak Ridge, Tennessee

ORO-5205-3
Distribution Category UC-91

CHARACTERIZATION AND ANALYSIS OF DEVONIAN SHALES AS RELATED TO RELEASE OF GASEOUS HYDROCARBONS

Quarterly Technical Progress Report
March 1977 - May 1977

M. Jack Snyder and J. R. Schorr

Date Published - May 31, 1977

Under Contract No. E(40-1)-5205

PREPARED FOR THE
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

CHARACTERIZATION AND ANALYSIS OF DEVONIAN SHALES
AS RELATED TO RELEASE OF GASEOUS HYDROCARBONS

Quarterly Technical Progress Report
March 1977 - May 1977

INTRODUCTION

This program which is a part of The Resource Inventory and Shale Characterization subprojects of ERDA's Eastern Shale Project, was initiated in September 1976 with an effective contract period of July 1, 1976 through September 30, 1977. During July and August, in anticipation of the execution of the contract, work was started in connection with the sampling of cores from Devonian shale wells which had been or were being drilled and cored. Active laboratory work was started in September. This third quarterly technical progress report covers progress made in the quarter from March 1977 through May 1977.

OBJECTIVE AND SCOPE

The objective of this program is to determine the relationships between shale characteristics, hydrocarbon gas content, and well location to provide a sound basis for defining the productive capacity of the Eastern Devonian shale deposits and for guiding research, development, and demonstration projects to enhance the recovery of natural gas from the shale deposits. The program includes a number of elemental tasks as a part of the Resource Inventory and Shale Characterization subprojects of ERDA's Eastern Shale Project and is designed to provide large quantities of support data for that project.

Approximately 1000 core samples of gas bearing Eastern Devonian shale will be examined in the program. After the characterization data for individual wells have been compiled, a regression-type analysis for

pattern recognition will be performed to establish the interrelationship between the shale characteristics, the hydrocarbon gas content, and well locations from which the samples were obtained.

The work during the first 18-month period of this program comprises six tasks:

Task	Descriptive Title
1	Core Sampling
2	Gas Content and Gas Release Kinetics
3	Chemical Characterization of Shale
4	Physical Characterization of Shale
5	Lithology of Shale
6	Data Interpretation and Correlation

Task 1. Core Sampling

In cooperation with representatives of ERDA and of the cognizant State Geological Survey or The U.S. Geological Survey, (1) participate in the selection of core samples for characterization in the Battelle program, and (2) encapsulate the selected samples in special sealed containers to preserve their approximate "down-hole" condition and gather relevant information from on-site observations and well-log data for subsequent interpretation and correlation with characterization results on the selected samples.

Task 2. Gas Content and Gas Release Kinetics

Determine the composition of and quantity of hydrocarbon gas evolved from and surrounding the shale samples in the sealed containers. Determine the gas release kinetics by observations of the rate of pressure build-up in the sealed containers after initial release of pressure for selected samples having high initial pressures and by thermal gravimetric

measurement of weight loss as a function of time at three different temperatures for specimens cut from the samples after removal from the sealed containers.

Task 3. Chemical Characterization of Shale

Determine total carbon, hydrogen, and nitrogen contents and, where appropriate, total carbonate content for all samples. Determine trace elements by optical emission spectroscopy on selected samples from each well.

Task 4. Physical Characeterization of Shale

Characterize the microstructure of the samples in terms of porosity (total, open, and closed), pore size distribution, total surface area, and gas permeability.

Task 5. Lithology of Shale

Determine the mineralogical composition of the samples by x-ray diffraction techniques and define the morphology of the minerals and their relationship to the organic debris by thin-section petrography. Ascertain structural changes resulting from heating by observations on duplicate samples from the same core sample. Examine selected samples from each well by scanning electron microscopy to supplement the petrographic observations.

Task 6. Data Interpretation and Correlation

Compile the data from the field observations, well logs, and laboratory characterizations and observations into a data package for each well for input to the regression-type analysis, for input to the USGS data bank, and for transmission to the ERDA technical project officer. Determine, using a pattern recognition, statistical analysis

technique and conventional data interpretation methods, the interrelationships and trends between the hydrocarbon gas content at various levels, the well head observation, and the lithological, chemical, and physical characteristics of the shale for individual wells and as a function of location.

SUMMARY OF PROGRESS

A milestone chart showing the planned progress on the various tasks is given in Figure 1 and the status of the sampling and characterization tasks are summarized in Table 1. The program is generally on schedule, but some unanticipated difficulties in a few of the characterization experiments and anomalous results in others have caused some minor schedule slippage during the present quarter.

DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Task 1. Core Sampling

Another well was sampled during this quarter. The well is located near Norton, Wise County, Virginia. Core point was reached on April 22 and coring was completed on April 29, 1977. The total depth sampled was from 4871 through 5469 feet; cores were taken and samples selected at two intervals: 4871-4980 feet, 5211-5469 feet. A total of 81 samples were canned for examination by BCL and other ERDA contractors. A summary of the pertinent information about all of the wells sampled to date is given in Table 2.

Many of the core sections from the Wise County, Virginia well exhibited considerable outgassing during the initial examination and many of the cans bulged noticeably within a few hours after sealing. All canned samples for BCL and for Mound Laboratory were checked at BCL for gas leaks approximately two weeks after canning and leaks were detected in 16 out of the 72 samples. As is discussed in the next section of this report, we

	1976						1977								
ITEM	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP
Quarterly Progress Report	Δ					∇			∇			∇			∇
Core Sampling	Δ														
Samples Taken	25	124	148	148	265	265	265	280	280	320	320	340	340	360	380
Wells Sampled	1	1	3	3	4	4	4	5	5	6	6	7	7	8	9
Gas Content and Release			Δ												
Initial Off-Gas Analyses				7	29	54	74	81	88	110	130	150	175	200	225
Kinetics of Gas Release						4	6	6	6	10	25	45	65	90	115
Chemical Characterization					Δ										
C, H, N Analysis						6	26	40	62	65	85	130	160	190	220
Optical Emission Spectroscopy									12	13	13	14	15	16	17
Physical Characterization			Δ												
Density/Porosity							9	41	72	100	120	140	165	190	220
Pore Size										2	15	30	55	80	105
Surface Area						10	10	10	21	40	50	60	75	100	125
Permeability											5	10	20	35	55
Lithology						Δ									
XRD								3	3	5	10	15	20	30	40
Petrographic Examination											10	10	10	15	40
Heat Treatment Followed by Petrographic											5	5	5	10	20
All Characterizations Completed													Δ		
Individual Samples													10	15	40
Individual Wells														1	2
Data Interpretation and Correlation				Δ											
Correlation Procedures Established				Δ								∇			
Correlation Within an Individual Well									Δ					∇	
Correlation Between Two or More Wells										Δ					∇

Note: Numbers are cumulative numbers of samples or wells completed at end of month indicated. Actual numbers are shown through March. Goals are shown for succeeding months.

Δ Start of Activity

∇ Completion of Activity

FIGURE 1. MILESTONE CHART - REVISED MAY 1977

TABLE 1. QUARTERLY PROGRESS ON SAMPLING AND CHARACTERIZATION TASKS

Item	Cumulative Number Completed at End of Quarter: 1st Quarter July-Nov. 1976	2nd Quarter Dec. 1976-Feb. 1977	3rd Quarter Mar. 1977-May 1977
Core Sampling			
Samples Taken	265	280	320
Wells Sampled	4	5	6
Gas Content and Release			
Initial Off-Gas Analysis	29	81	110
Kinetics of Gas Release	0	6	6
Chemical Characterization			
C, H, N Analysis	0	40	62
Optical Emission Spectroscopy	0	0	12
Physical Characterization			
Density/Porosity	0	41	91
Pore Size	0	0	1
Surface Area	0	10	77
Permeability	0	0	2
Lithology			
XRD	0	0	3
Petrographic Examination	0	0	5
Heat Treatment/Petrography	0	0	4
All Characterizations Complete			
Individual Samples	0	0	0
Individual Wells	0	0	0

TABLE 2. IDENTIFICATION OF CORED WELLS AND SAMPLES SELECTED

Well Code Number	Location of Well	Well Operator	Date Sampled	Core Depth Interval, Feet	Number of Samples
C-1	Lincoln County, WV	Columbia Gas	Jan. 1976	2746 - 4045	82
C-2	Lincoln County, WV	Columbia Gas	Jan. 1976	2655 - 3971	17
R-109	Washington County, OH	River Gas	Jul. 30, 1976	3494 - 3705	25
P-1	Sullivan County, IN	Energy Resources of Indiana, Inc.	Sept. 1, 1976	2495 - 2595	11[a]
O-1	Christian County, KY	Orbit Gas	Sept. 18, 1976	2183 - 2319	13[b]
C-336	Martin County, KY	Columbia Gas	Nov. 6, 1976	2434 - 3405	117[c]
T-1	Effingham County, IL	Tri-Star	Feb. 13-18, 1977	3006 - 3106	15[d]
C-338	Wise County, VA	Columbia Gas	Apr. 22-30, 1977	4871 - 5469	40[e]

(a) An additional 6 samples were selected and encapsulated for other ERDA contractors.

(b) An additional 4 samples were selected and encapsulated for other ERDA contractors.

(c) An additional 90 samples were selected and encapsulated for other ERDA contractors.

(d) An additional 16 samples were selected and encapsulated for other ERDA contractors.

(e) An additional 41 samples were selected and encapsulated for other ERDA contractors.

suspect that many of the canned samples from the other wells may have leaked prior to the initial gas analyses. Potential methods of correcting for the amount of gas lost and of avoiding the problem in future sampling are being investigated.

Task 2. Gas Content and Gas Release Kinetics

Additional data were collected on the initial pressure, volume, and composition of the gas released into the free air space surrounding the sealed shale samples, following the procedures described in the first quarterly report.(1) A total of 110 canned samples, including all samples from Wells O-1, P-1, C-2, and R-109, have been tapped and the released gas has been measured and analyzed. Initial gas release analyses have also been completed on selected samples from all of the other wells, including some of those from the most recent well which were leaking or were bulging excessively. The data are given in Tables 3 and 4.

A detailed examination of the gas analysis data reveals a number of anomalies. Many samples exhibit high concentrations of total hydrocarbon gases and low concentrations of nitrogen and oxygen, but low gas pressures. For example, the gas analysis results for Sample R-109-3526 (Table 4) show the total hydrocarbon content in the free space is 90.4 per cent, the nitrogen content is 8.56 percent and the oxygen content is 0.54 percent. If we assume that the composition of the gas in the free space was 80 percent nitrogen and 20 percent oxygen at the time of sealing, the pressure at the time of tapping should have been about 7100 Torr. The measured pressure was 740 Torr, an order of magnitude low. A comparison of the measured pressures with the expected pressures calculated from the gas analysis data, for those wells on which all samples have been tapped (Tables 5 though 7), revealed that a substantial number (about 62 percent) of the samples had significantly low measured pressures.

There are four possible explanations for the anomalous pressure data: (1) leakage, (2) outgassing during the time that the core is placed in the can and before it is sealed with the result that the initial gas composition is a mixture of air and hydrocarbon gases, (3) adsorption of

---

(1) ORO-5205-1, "Characterization and Analysis of Devonian Shales As Related to Release of Gaseous Hydrocarbons", M. Jack Snyder and J. R. Schorr (December 1, 1976).

TABLE 3. DATA FROM INITIAL GAS RELEASE MEASUREMENTS ON WELLS C-1, C-2, C-336, AND C-338

	PRES	GAS CONTENT, VOLUME PERCENT									
SAMPLE ID	TORR	METH	ETHA	PROP	BUTA	PENT	NITR	OXYG	CHGS	MGAS	SEQ
C- 1-2746.	750.	79.21	18.33	2.42	0.00	0.00	0.00	0.00	99.96	79.24	1
C- 1-2927.A	760.	41.00	10.00	5.60	1.60	.30	37.00	3.30	58.70	69.85	13
C- 1-2999.	870.	40.16	4.61	1.92	.58	.18	49.64	.90	47.45	84.64	20
C- 1-3085.	750.	27.93	4.62	2.01	.80	.32	58.73	2.16	35.68	78.28	23
C- 1-3175.	1110.	30.05	6.97	3.68	.92	.24	56.37	.71	41.86	71.79	33
C- 1-3198.Z	1025.	46.80	11.90	5.50	.74	.81	35.00	.43	65.75	71.18	35
C- 1-3396.	970.	29.70	5.20	2.50	.80	.20	59.40	1.20	38.40	77.34	51
C- 1-3426.	930.	58.40	14.98	12.27	3.42	.82	8.09	1.33	89.89	64.97	52
C- 1-3573.	950.	59.19	16.66	9.86	2.93	.72	9.77	.20	89.36	66.24	59
C- 1-3593.	752.	35.90	8.50	3.60	1.20	.18	47.00	1.40	49.38	72.70	62
C- 1-3651.	1000.	57.59	17.45	10.14	2.54	.53	10.85	0.00	88.25	65.26	66
C- 1-3701.	1060.	58.65	15.81	7.87	1.74	.37	12.17	1.97	84.44	69.46	67
C- 1-3869.	1060.	55.49	21.20	12.37	2.64	.50	6.25	.37	92.20	60.18	79
C- 1-3998.	1020.	47.42	9.98	4.09	1.00	.10	34.68	.42	62.59	75.76	65
C- 1-4045.	840.	63.93	18.19	10.98	2.31	.45	2.73	.92	95.86	66.69	86
C- 2-2655.	740.	8.47	.81	.28	0.00	0.00	85.33	1.35	9.56	88.60	1
C- 2-2710.	750.	11.87	1.36	.63	.04	0.00	82.60	1.36	13.90	85.40	2
C- 2-2761.	740.	12.69	1.81	.99	.10	0.00	81.15	1.37	15.59	81.40	3
C- 2-3000.	925.	25.88	3.36	1.84	.53	.20	64.57	.83	31.81	81.36	4
C- 2-3025.	920.	23.08	4.31	3.81	.77	.17	63.72	.72	32.14	71.81	5
C- 2-3050.	890.	22.63	3.15	1.56	.38	0.00	67.86	1.05	27.72	81.64	6
C- 2-3101.	1100.	32.88	5.98	2.54	.66	.34	54.70	.73	42.40	77.55	7
C- 2-3303.	750.	19.58	4.09	2.92	.54	.21	68.50	.99	27.34	71.62	8
C- 2-3328.	720.	23.98	5.88	3.42	.74	.16	58.95	2.60	34.18	70.16	9
C- 2-3378.	830.	54.10	15.10	13.05	3.11	.76	12.67	.35	86.12	62.82	10
C- 2-3428.	780.	47.29	10.47	6.31	2.07	.47	32.17	.67	66.61	71.00	11
C- 2-3478.	845.	16.34	2.87	1.56	.51	.12	69.99	7.12	21.40	76.36	12
C- 2-3528.	760.	57.76	15.82	10.01	2.75	.78	11.05	.98	87.12	66.30	13
C- 2-3896.	990.	47.48	13.59	7.72	1.77	.48	26.98	.46	71.04	66.84	14
C- 2-3922.	750.	46.33	20.46	13.27	3.96	.99	13.64	.69	85.01	54.50	15
C- 2-3961.	955.	65.19	18.39	9.79	2.05	.44	3.69	.10	95.86	68.01	16
C- 2-3971.	775.	59.08	17.93	11.27	2.10	.33	7.38	1.54	90.77	65.09	17
C-336-2524.	775.	6.70	1.60	.05	.01	0.00	79.60	9.50	8.36	80.14	11
C-336-2637.	750.	.21	.19	0.00	0.00	0.00	78.39	21.21	.40	52.50	24
C-336-2773.	750.	1.76	.91	1.08	.66	.25	76.08	17.36	4.66	37.77	41
C-336-2852.	750.	3.30	1.50	1.10	.03	.09	78.10	13.80	6.02	54.82	51
C-336-2960.	950.	28.27	8.53	6.29	1.64	.44	49.41	3.21	45.17	62.59	63
C-336-2960.Z	840.	25.23	7.85	5.47	1.39	.31	52.92	5.26	40.25	62.68	64
C-336-2999.	750.	4.00	.90	1.10	.70	.23	76.58	15.91	6.93	57.72	68
C-336-3038.	750.	12.31	4.91	3.20	4.19	3.13	59.12	10.65	27.74	44.38	73
C-336-3069.	1470.	36.62	9.10	6.02	1.73	.49	41.97	2.20	53.96	67.87	76
C-336-3069.Z	900.	27.93	6.52	3.31	1.04	.26	54.61	4.98	39.06	71.51	77
C-336-3186.	750.	11.04	2.43	1.94	.29	.06	71.98	9.89	15.76	70.05	90
C-336-3186.Z	800.	7.12	1.57	.73	.18	.06	78.30	9.16	9.66	73.71	91
C-336-3216.	810.	7.31	1.45	.42	.16	.23	76.05	14.02	9.57	76.38	95
C-336-3254.	840.	10.58	1.74	.82	.10	.02	74.21	10.64	13.26	79.79	100
C-336-3325.	840.	20.13	5.36	3.68	1.08	.37	60.39	7.55	30.62	65.74	109
C-338-4892.	1907.	64.50	6.70	.86	.08	0.00	25.10	2.80	72.14	89.41	3
C-338-4902.	1450.	63.40	7.63	.95	0.00	0.00	26.10	1.93	71.98	88.08	4
C-338-5303.	2900.	77.50	4.78	.44	0.00	0.00	16.70	.33	82.72	93.69	22
C-338-5342.	1225.	72.10	6.80	.61	0.00	0.00	19.80	.59	79.51	90.68	26
C-338-5362.	1150.	73.90	7.91	.63	.06	0.00	16.70	.33	82.50	89.58	29
C-338-5372.	975.	78.30	8.50	.70	0.00	0.00	11.30	.57	87.50	89.49	30
C-338-5382.	1000.	66.60	6.70	.61	0.00	0.00	23.10	2.80	73.91	90.11	31
C-338-5404.	850.	51.03	6.35	.75	.07	0.00	36.55	4.96	58.20	87.68	33
C-338-5414.	1490.	62.90	6.10	.47	0.00	0.00	26.47	4.01	69.47	90.54	34
C-338-5424.	2600.	69.85	5.71	.41	0.00	0.00	21.55	2.38	75.97	91.94	35
C-338-5434.	1125.	55.20	5.80	.66	0.00	0.00	34.50	3.60	61.66	89.49	36
C-338-5444.	1125.	71.30	7.50	.55	0.00	0.00	18.80	1.57	79.35	89.86	37
C-338-5457.	975.	56.30	5.10	.36	0.00	0.00	32.00	6.20	61.76	91.16	39

TABLE 4. DATA FROM INITIAL GAS RELEASE MEASUREMENTS ON WELLS 0-1, P-1, R-109, AMD T-1

	PRES	GAS CONTENT, VOLUME PERCENT									
SAMPLE ID	TORR	METH	ETHA	PROP	BUTA	PENT	NITR	OXYG	CHGS	MGAS	SEQ
O- 1-2183.	800.	81.55	6.11	1.10	.11	0.00	11.01	0.00	88.87	91.76	1
O- 1-2191.	2150.	67.21	4.47	1.03	.09	0.00	24.77	1.91	72.80	92.32	2
O- 1-2220.	1100.	35.65	2.79	1.05	.21	.02	52.99	5.18	39.72	89.75	3
O- 1-2230.	1000.	27.40	1.89	.07	.09	.02	61.04	7.73	29.46	93.01	4
O- 1-2239.	1750.	57.44	3.90	1.18	.21	0.00	34.88	.96	62.73	91.57	5
O- 1-2251.	850.	25.30	2.00	.40	.02	0.00	64.00	6.90	27.72	91.27	6
O- 1-2259.	2100.	69.12	2.93	1.83	.05	0.00	24.16	1.43	73.98	93.43	7
O- 1-2271.	1370.	50.46	2.78	2.30	.06	0.00	40.98	2.26	55.60	90.76	8
O- 1-2281.	1690.	59.93	2.17	0.00	0.00	0.00	34.19	2.68	62.10	96.51	9
O- 1-2290.	1200.	43.46	1.78	0.00	0.00	0.00	48.30	5.45	45.24	96.07	10
O- 1-2300.	1225.	43.40	1.97	0.00	0.00	0.00	48.41	4.93	45.37	95.66	11
O- 1-2310.	1250.	46.64	1.88	0.00	0.00	0.00	45.21	5.15	48.52	95.13	12
O- 1-2319.	960.	71.57	2.45	0.00	0.00	0.00	24.12	.84	74.02	96.69	13
P- 1-2495.	900.	21.47	4.61	3.53	1.72	.63	65.87	.91	31.96	67.18	1
P- 1-2505.	1345.	66.41	3.60	.22	0.00	0.00	21.06	2.18	70.23	94.56	2
P- 1-2515.	1900.	58.46	4.19	.26	.05	0.00	29.95	2.68	62.96	92.85	3
P- 1-2528.	2104.	60.60	2.59	0.00	0.00	0.00	28.14	1.88	63.19	95.90	4
P- 1-2536.	1770.	54.60	2.27	1.65	0.00	0.00	31.29	2.31	58.52	93.30	5
P- 1-2547.	1700.	61.32	6.01	.20	0.00	0.00	27.72	.54	67.53	90.80	6
P- 1-2554.	1900.	62.95	5.42	.34	.07	.03	27.23	.65	68.81	91.48	7
P- 1-2565.	1390.	52.58	5.04	1.63	.59	.29	35.62	.74	60.13	87.44	8
P- 1-2575.	1970.	62.81	4.60	0.00	0.00	0.00	27.33	.12	67.41	93.18	9
P- 1-2585.	1340.	45.00	3.30	0.00	0.00	0.00	40.40	4.10	48.30	93.17	10
P- 1-2595.	2030.	59.01	4.95	2.36	.99	.30	26.58	.56	67.60	87.29	11
R-109-3494.	860.	30.81	10.10	7.04	2.26	.52	47.92	.86	50.73	60.73	1
R-109-3506.	925.	61.86	11.38	5.53	1.29	.45	5.91	.38	80.61	76.74	2
R-109-3516.	775.	61.81	12.82	7.48	2.05	.46	14.49	.71	84.62	73.04	3
R-109-3526.	740.	68.73	12.52	6.59	2.12	.45	8.56	.54	90.41	76.02	4
R-109-3536.	750.	32.81	6.56	2.79	.68	.29	50.30	5.72	43.13	76.07	5
R-109-3545.	750.	37.55	7.03	3.05	.91	.32	42.63	3.64	48.96	76.90	6
R-109-3555.	730.	50.15	13.72	8.71	2.16	.53	22.49	1.94	75.27	66.63	7
R-109-3564.	740.	65.28	14.55	7.65	2.16	.46	8.38	1.53	90.10	72.45	8
R-109-3575.	875.	68.46	10.30	3.45	1.11	.33	15.80	.11	83.65	81.84	9
R-109-3585.	745.	35.54	8.40	3.50	1.70	.47	45.93	4.11	49.71	71.49	10
R-109-3593.	950.	37.65	6.60	2.51	.82	.39	46.53	4.47	47.97	78.49	11
R-109-3605.	750.	62.31	13.54	7.57	2.13	.55	12.75	.77	86.10	72.37	12
R-109-3606.A	740.	49.47	12.97	7.05	2.52	.50	24.04	2.85	72.51	68.23	13
R-109-3606.B	930.	26.16	6.66	4.25	1.19	.30	55.13	3.78	38.56	67.94	14
R-109-3616.	1050.	40.65	6.57	2.95	.85	.23	45.90	.85	51.25	79.32	15
R-109-3626.	775.	48.04	8.18	3.08	.86	.20	38.00	.57	60.36	79.59	16
R-109-3634.	750.	53.84	7.37	2.43	.70	.19	32.97	1.44	64.53	83.43	17
R-109-3644.A	1120.	34.19	6.20	2.36	.68	.27	51.37	3.42	43.70	78.24	18
R-109-3644.B	825.	14.27	3.57	1.98	.50	.16	69.69	7.57	20.48	69.68	19
R-109-3665.	2165.	60.51	13.65	6.98	1.88	.36	15.85	.17	83.38	72.57	20
R-109-3675.	760.	66.65	14.98	6.55	1.90	.74	8.83	.11	90.82	73.39	21
R-109-3685.	1300.	60.95	10.76	4.86	1.52	.43	20.25	.71	78.52	77.62	22
R-109-3695.	1745.	47.53	8.49	7.41	1.04	.26	32.56	1.70	64.73	73.43	23
R-109-3705.	730.	18.11	3.60	1.99	.49	.18	50.83	7.61	24.37	74.31	24
R-109-3711.	860.	19.02	4.60	2.02	.65	.17	68.06	4.29	26.46	71.88	25
T- 1-3012.	750.	2.36	.81	.40	.20	0.00	79.01	16.62	3.77	62.60	1
T- 1-3022.	750.	9.73	2.90	1.24	.66	.08	71.61	13.70	14.61	66.60	2
T- 1-3043.	825.	4.39	1.35	.50	.21	.02	76.88	14.65	6.47	67.85	3

TABLE 5. COMPARISON OF MEASURED GAS PRESSURE WITH EXPECTED PRESSURE CALCULATED FROM NITROGEN CONTENT, WELL C-2

Sample Number	Pressure, Torr		
	Measured	Calculated	Measured/Calculated
C-2 - 2655	740	710	1.04
C-2 - 2710	750	735	1.02
C-2 - 2761	740	750	0.99
C-2 - 3000	925	945	0.98
C-2 - 3025	920	960	0.96
C-2 - 3050	890	900	0.99
C-2 - 3101	1100	1110	0.99
C-2 - 3303	750	890	0.84
C-2 - 3328	720	1030	0.70
C-2 - 3378	830	4880	0.17
C-2 - 3428	780	1900	0.41
C-2 - 3478	845	870	0.97
C-2 - 3528	760	5430	0.14
C-2 - 3896	990	2250	0.44
C-2 - 3922	750	4410	0.17
C-2 - 3961	955	15915	0.06
C-2 - 3971	775	8610	0.09

TABLE 6. COMPARISON OF MEASURED GAS PRESSURE WITH EXPECTED PRESSURE CALCULATED FROM NITROGEN CONTENT, WELLS 0-1 AND P-1

	Pressure, Torr		
Sample Number	Measured	Calculated	Measured/Calculated
0-1 - 2183	800	5715	0.14
0-1 - 2191	2150	2445	0.88
0-1 - 2220	1100	1145	0.96
0-1 - 2230	1000	995	1.00
0-1 - 2239	1750	1745	1.00
0-1 - 2251	850	955	0.89
0-1 - 2259	2100	2530	0.83
0-1 - 2271	1370	1490	0.92
0-1 - 2281	1690	1775	0.95
0-1 - 2290	1200	1265	0.95
0-1 - 2300	1225	1250	0.98
0-1 - 2310	1250	1345	0.93
0-1 - 2319	860	2530	0.34
P-1 - 2495	900	920	0.98
P-1 - 2505	1345	2860	0.47
P-1 - 2515	1900	2020	0.94
P-1 - 2528	2104	2170	0.97
P-1 - 2536	1770	1945	0.91
P-1 - 2547	1700	2180	0.78
P-1 - 2554	1900	2235	0.85
P-1 - 2565	1390	1715	0.81
P-1 - 2575	1970	2215	0.89
P-1 - 2585	1340	1505	0.89
P-1 - 2595	2030	2280	0.89

TABLE 7. COMPARISON OF MEASURED GAS PRESSURE WITH EXPECTED PRESSURE CALCULATED FROM NITROGEN CONTENT, WELL R-109

Sample Number	Pressure, Torr Measured	Calculated	Measured/Calculated
R-109 - 3494	860	1265	0.68
R-109 - 3506	925	10480	0.09
R-109 - 3516	775	4305	0.18
R-109 - 3526	740	7100	0.10
R-109 - 3536	750	1210	0.62
R-109 - 3545	750	1440	0.52
R-109 - 3555	780	2435	0.32
R-109 - 3564	740	7250	0.10
R-109 - 3575	875	3805	0.23
R-109 - 3585	745	1330	0.56
R-109 - 3593	950	1300	0.73
R-109 - 3605	750	4690	0.16
R-109 - 3606 A	740	2550	0.29
R-109 - 3606 B	930	1180	0.79
R-109 - 3616	1050	1250	0.84
R-109 - 3626	775	1615	0.48
R-109 - 3634	750	1830	0.41
R-109 - 3644 A	1120	1180	0.95
R-109 - 3644 B	825	870	0.95
R-109 - 3665	2165	3865	0.56
R-109 - 3675	760	6885	0.11
R-109 - 3685	1300	3025	0.43
R-109 - 3695	1745	1875	0.93
R-109 - 3705	730	1195	0.61
R-109 - 3711	860	895	0.96

air by the shale as hydrocarbon gas is released, and (4) a combination of these. In view of the observed leaking of several cans from the most recent well, leakage is probably responsible for some of the observed low pressures and is highly probable for those samples where the final pressure is near atmospheric. However, there are several samples in which the observed pressure, while less than 90 percent of the calculated pressure, is still well above atmospheric (1000 to 2000 Torr). For such samples the leak rate must be very low or the leak must be intermittent (perhaps leaking at higher pressures but sealing at the measured pressure), or the calculated pressure loss must be a result of some factor other than leakage. The most likely explanation in these cases is that outgassing during the canning operation resulted in an air-gas mixture containing significant amounts of hydrocarbon gas in the free space surrounding the shale sample at the time of sealing.

Although it is conceivable that some exchange of air for hydrocarbon gas within the pores of the shale could occur, the amount of pressure loss resulting from such an exchange is negligible. For example, the open pore volume in the shale sample discussed earlier is only about 6 percent of the free space in the can; hence, even complete filling of the pores by air would account for only a 6 percent loss in pressure.

Investigations are underway to determine how many of the canned samples which have not yet been tapped are leaking and to compare the pressure and composition data from cans that are known to be leaking with data from cans that are known not to be leaking. Other methods of encapsulating samples which will insure against leakage in future runs are under consideration. Plans are being formulated to collect data on the pressure and gas composition of selected samples at the well site as quickly as possible after sealing and to monitor changes in pressure and composition from the time of sealing until the cans are opened in the laboratory.

Discussions at the recent workshop on gas release characteristics (held at MERC on May 5, 1977) revealed that the four laboratories involved in these studies (Battelle-Columbus, Columbia Gas, Mound, and Juniata College) follow essentially the same analytical procedures but use different equations in calculating the amount of gas released from the shale. Using Battelle gas analysis data on samples from Wells C-2, O-1, P-1, and R-109 the amount

of gas released per unit volume of shale was calculated from the equations used by Columbia Gas and Juniata College.[2] The results are compared in Figures 2 and 3 with values calculated from the same data using the Battelle equations for total gas volume in the free space at STP (compared with the value resulting from Columbia's equation) and for the released hydrocarbon gas volume at STP (compared with the values resulting from Juniata's equation). In both cases the relationships are reasonably linear over the range of values encountered in these wells and values reported by one laboratory can be multiplied by an appropriate constant to calculate equivalent values for another laboratory without introducing serious error. It is suggested that each laboratory report all of the primary data from the off-gas analysis: pressure and temperature at time of tapping, free space volume, bulk volume of shale, porosity of shale, and composition of gas. If this is done, the amount of gas released at the time of tapping can be calculated by any of the equations and the integration or comparison of data from the various laboratories will be simplified.

Task 3. Chemical Characterization of Shale

Optical emission spectroscopic analyses have been completed on the planned number of samples from the three high priority wells (O-1, P-1, and C-2) and from Wells C-1 and R-109. The data (Table 8) do not reveal any unexpected or significant differences in major chemical composition nor in the presence of trace elements. Chemical analyses for total carbon, hydrogen, and nitrogen have been completed on most of the samples from the three high priority wells and several samples from C-1 and R-109. Low-temperature ashing analyses on the samples having higher carbon content have resulted in some anomalous values and the procedure is being re-examined.

Task 4. Physical Characterization of Shale

Density measurements and porosity calculations have now been completed on 91 samples. Some anomalous values are being rechecked. Surface

---

(2) The calculation procedure used by Mound Laboratory is believed to be essentially the same as that used by Battelle-Columbus.

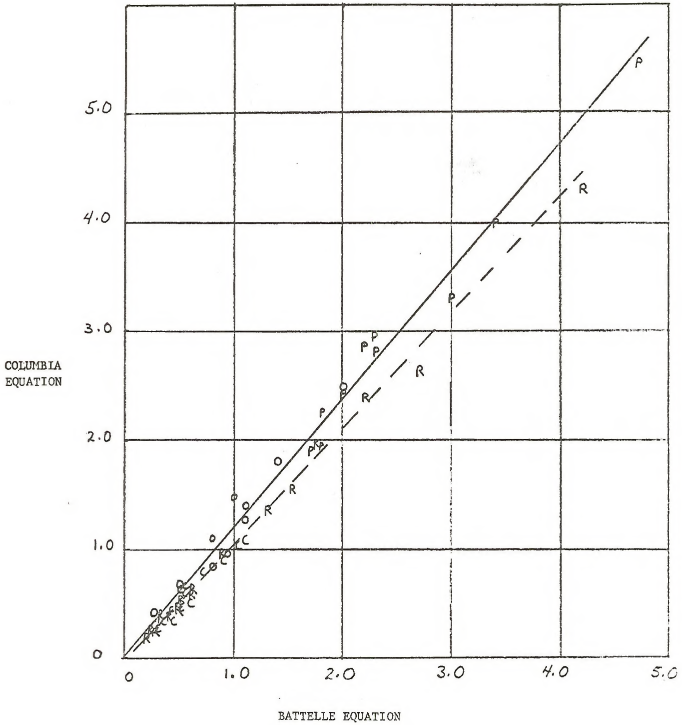

FIGURE 2. COMPARISON OF CALCULATED VALUES FOR GAS RELEASED PER UNIT VOLUME OF SHALE USING BATTELLE AND COLUMBIA EQUATIONS

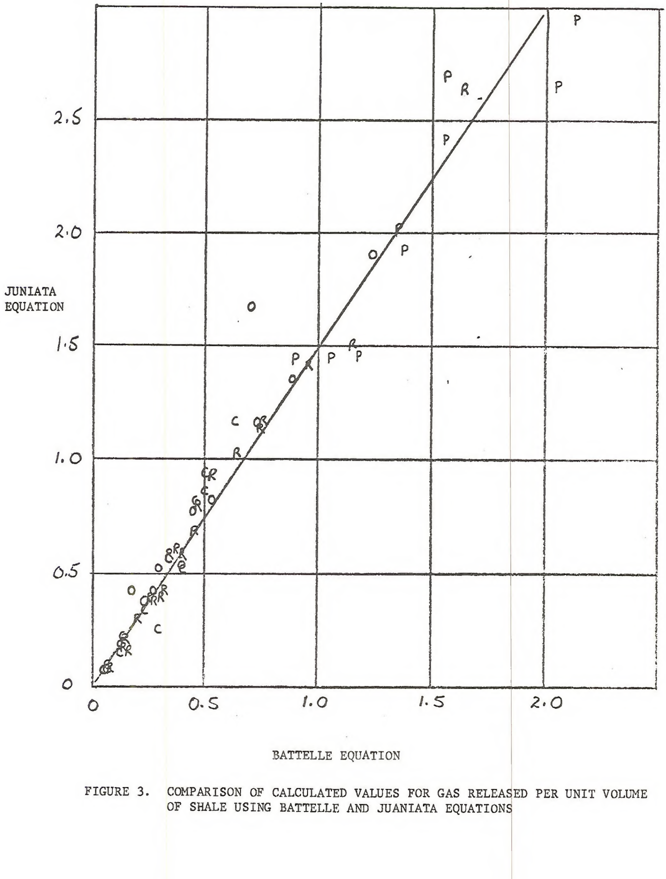

FIGURE 3. COMPARISON OF CALCULATED VALUES FOR GAS RELEASED PER UNIT VOLUME OF SHALE USING BATTELLE AND JUANIATA EQUATIONS

TABLE 8. RESULTS OF OPTICAL EMISSION SPECTROSCOPIC ANALYSES

Sample Number	Elements Detected, Approximate Weight Percent																
	Si	Fe	Al	Mg	K	Na	Ca	Ti	Ni	Mo	Mn	Ba	B	Pb	V	Cu	Zr
C-1-3573	10-20	4-8	5-10	.5-1	3-5	.5	.4	.3	.005	.005	.02	.03	.01	< .01	.01	.01	.01
C-1-3651	10-20	4-8	5-10	.5-1	3-5	.5	.3	.3	.005	.005	.02	.03	.02	.01	.01	.03	.01
C-1-3701	10-20	4-8	5-10	.5-1	3-5	.5	.1	.3	.01	.01	.02	.03	.01	.01	.02	.03	.01
C-1-4045	10-20	4-8	5-10	.5-1	3-5	.5	1.	.3	.01	.005	.02	.02	.02	< .01	.03	.01	.01
C-2-3528	10-20	4-8	5-10	.5-1	3-5	.5	.4	.3	.005	.005	.02	.03	.01	< .01	.01	.01	.01
O-1-2259	10-20	4-8	5-10	.5-1	3-5	.5	1.	.3	.02	.02	.02	.02	.03	< .01	.04	.01	.01
O-1-2271	10-20	6-10	5-10	1-3	3-5	.5	4-8	.3	.005	<.005	.03	.02	.01	< .01	.01	.02	.01
P-1-2205	10-20	4-8	5-10	.5-1	3-5	.5	.3	.3	.01	<.005	.01	.02	.01	< .01	.04	.02	.01
P-1-2515	10-20	4-8	5-10	.5	3-5	.5	.1	.3	.005	<.005	.005	.02	.01	< .01	.02	.01	.01
P-1-2536	10-20	6-10	5-10	1.	3-5	.5	3-5	.3	.005	.01	.03	.02	.01	< .01	.01	.01	.01
P-1-2554	10-20	4-8	5-10	1.	3-5	.5	1.	.3	.005	<.005	.02	.03	.01	< .01	.01	.01	.01
R-109-3606A	10-20	4-8	5-10	.5-1	3-5	.5	.4	.3	.005	<.005	.02	.03	.01	< .01	.01	.01	.01

area measurements using the Strohleim Area Meter have been completed on 77 samples, including all of the samples from the three high priority wells. Some re-runs of selected samples are being made using another apparatus to assess the reliability of the Strohleim data and to examine the effects of degassing conditions on the measured surface area.

Task 5. Lithology of Shale

Initial results of x-ray diffraction runs on single samples from the three high-priority wells did not reveal any significant well-to-well differences. As expected from previous examinations of Devonian shales, the major mineral phases identified were quartz, muscovite, pyrite, and illite. The procedures used in the analyses are being re-examined to determine whether more quantitative data can be obtained by minor modifications in sample preparation.

Four shale samples, two from C-1 and one each from O-1 and C-2 were examined in powder and thin-section form using the petrographic microscope and SEM photographs and energy-dispersive analyses (EDAX) were obtained. The results of the petrographic examination of the powder samples are summarized in Table 9. It should be noted that only phases thought to be present in significant amounts were sought in the microscopic examination; other minerals known to be commonly present in shales in small quantities, such as zircon and apatite, and clay minerals other than illite were possibly present in the samples examined.

Thin sections from paired samples, one unheated and one heated at 900 F (480 C) for 1-1/2 hours were examined. The results are shown in Table 9.

Sample No. C-1-2927A

Strata in the section consisted of (1) clear illite layers containing little or no opaque pyrite grains nor cloudy organic material, (2) an illite matrix containing much organic material and some pyrite grains, and (3) layers intermediate between (1) and (2). In general, as the population density of pyrite grains increased, the opacity of the cloudy organic material increased.

TABLE 9. MINERAL CHARACTERISTICS IN SHALE SAMPLES

Sample No.	Minerals and Characteristics
C-1-2927A	Major - Illite - 15 μm average platelet size
	Major - Pyrite - 10 μm average grain size; range 4-45 μm
	Quartz or feldspar content very low; 20-25 μm grain size
C-1-3998	Major - Illite - ~ 7 μm average platelet size
	Major - Pyrite - 5-10 μm grain size
	Minor - Quartz or feldspar; 15-25 μm grain size
C-2-3000	Major - Illite - 25 μm average platelet size
	Major - Pyrite - 10 μm grain size
	Minor - Quartz or feldspar; 25-35 μm grain size
0-1-2259	Major - Illite - 10 μm average platelet size
	Major - Pyrite - 10 μm grain size
	Major - Dolomite - single-crystal fragments up to 60 μm across
	Minor - Quartz or feldspar; 20 μm grain size

Clear brown elongated shapes, taken to be spores, were observed but were not common.

Heated and unheated sections appeared similar regarding occurrence of opaque grains, cloudiness, and spores.

Sample No. C-1-3998

This section was lacking in contrasting strata of different components. Opaque, pyrite grains occurred singly, in clusters, and strung out in sheets within the illite matrix. Clouded areas, sometimes surrounding and sometimes not associated with the pyrite grains were common.

An unusual feature was the occurrence of well-formed circular areas of cloudiness without any apparent relation to other components such as grains or bedding planes. Diameter of these near-perfect circular areas ranged from ~125 μm downward. (The smaller ones could be small due to the section being cut through the cloudy bubble at some point other than the middle.)

The heated section differed from the unheated section in the absence of the circular cloudy areas.

Sample No. C-2-3000

This unheated section differed from all others in that it is light grey, uniform, and translucent. It consisted of a matrix of illite with a sparse distribution of opaque, sometimes octohedral, pyrite grains, and very little cloudy areas.

The section of the heated specimen had a greater content of pyrite grains and showed more dark cloudiness. The pyrite grains were commonly not isolated but occurred in long seams.

Sample No. 0-1-2259

The section showed stratification, with clear narrow bands free of opaque and cloudy material and broad bands with a high content of opaque

pyrite and cloudy material. The pyrite grains occurred sometimes as clusters but mostly as long seams parallel to the bedding plane.

The unheated section appeared similar to the heated section.

Table 10 shows the energy-dispersive analysis of the shale samples. The total counts ranged around 5000-6000 and were normalized to a total of 100 counts for comparison purposes. The table also gives some element ratios calculated from the number of counts per element. Some observations based on the data in this table follow:

(1) The presence of K, Al, Si, and of Fe and S in significant amounts supports the findings by petrographic microscope of illite and pyrite as major phases.

(2) The analyses strongly suggests that what was classed as quartz or feldspar in the petrographic examination was quartz. Lack of Na and Ca in the energy-dispersive analysis indicates an absence of Na- and Ca-containing feldspar (albite/anorthite). There is a K feldspar (orthoclase) though it commonly contains some Na.

(3) The very low quartz or feldspar content of Shale No. C-1-2927A, as observed in the microscopic examination of the powder sample, is confirmed by the lower Si count of this shale compared to the others.

(4) The variation in the Fe/S ratios from 1.2 to 4.0 suggests that what was called pyrite (FeS_2) may be pyrite in various stages of oxidation or simply a mixture of unoxidized pyrite per se or as a component in another Fe-bearing mineral.

The four samples examined exhibited some similarities and several differences in lithological characteristics:

<u>Similarities</u>

- All samples contained illite and pyrite as major phases.

TABLE 10. ENERGY DISPERSIVE ANALYSIS (EDAX)

Element Sample No.	Counts per 100 Counts Na	K	Ca	Mg	Al	Si	Fe	S	Ti	Fe/S	K/Al	K/Si	Al/Si
C-1-2927A	-	9.1	-	0.8	21.4	49.9	12.4	5.3	1.0	2.3	0.43	0.18	0.43
C-1-3998	Trace	8.7	-	1.2	18.7	63.3	5.0	2.6	0.6	1.9	0.47	0.14	0.30
C-2-3000	Trace	8.4	-	Trace	21.5	61.7	5.6	1.4	1.4	4.0	0.39	0.14	0.35
0-1-2259	Trace	11.0	-	Trace	17.9	60.6	6.1	3.1	1.2	2.0	0.61	0.18	0.30
C-1-2927A (Octahedrons)	-	1.4	1.4	-	7.8	18.5	38.0	32.9	-	1.2	0.18	0.08	0.42

- Particle size of the pyrite was similar in all samples.
- Particle size of the quartz or feldspar was similar in all samples.

Differences

- Sample No. C-1-2927A contained very little quartz or feldspar, unlike the other three samples.
- Sample No. 0-1-2259 contained dolomite, the other three did not.
- The coarseness of illite crystallization varies with each sample.
- Three of the four samples showed an Fe/S count ratio of around 2. Sample No. C-2-3000 had a ratio of 4, indicating Fe present in a different degree of oxidation.
- What were considered spores were observed in Sample No. C-1-2927A but not in the other three samples.
- An unidentified spherical cloudy feature was seen in Sample No. C-1-3998 but no in the other three samples.

Task 6. Data Interpretation and Correlation

The intrepretation and correlations that can be made with the data available at this stage of the investigation have been presented and discussed in the earlier sections of this report.

CONCLUSIONS

Only very limited and preliminary interpretation and correlations are justified on the basis of the limited amount of data and the tentative status of many of the data points. The data are not yet extensive enough to permit any conclusions to be drawn concerning the relationships between shale characteristics and gas release.